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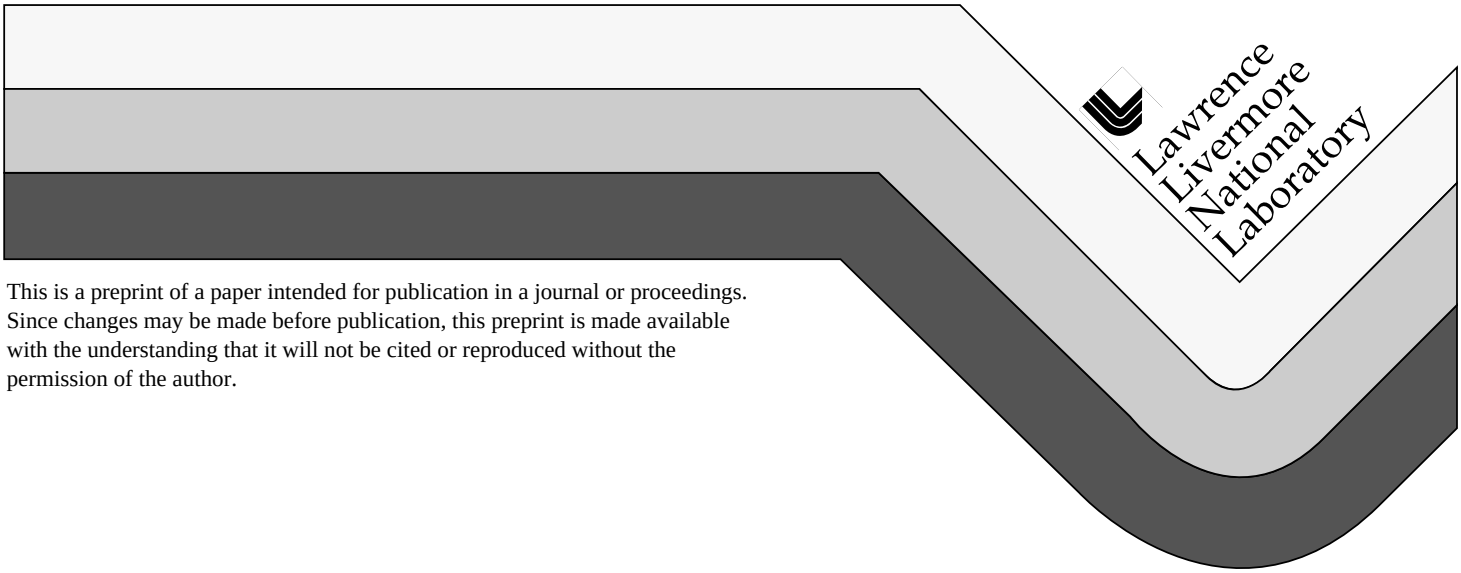

A QUANTITATIVE ASSESSMENT OF MICROBIOLOGICAL CONTRIBUTIONS TO CORROSION OF CANDIDATE NUCLEAR WASTE-PACKAGE MATERIALS

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ABSTRACT

The U.S. Department of Energy is contributing to the design of a potential nuclear-waste repository at Yucca Mountain, Nevada. A system to predict the contribution of Yucca Mountain (YM) bacteria to overall corrosion rates of candidate waste-package (WP) materials was designed and implemented. DC linear polarization resistance techniques were applied to candidate material coupons that had been inoculated with a mixture of YM-derived bacteria with potentially corrosive activities or left sterile. Inoculated bacteria caused a 5- to 6-fold increase in corrosion rate of carbon steel C1020 (to approximately 7–8μm/yr) and an almost 100-fold increase in corrosion rate of Alloy 400 (to approximately 1μm/yr). Microbiologically influenced corrosion (MIC) rates on more resistant materials (CRMs: Alloy 625, Type 304 Stainless Steel, and Alloy C22) were on the order of hundredths of micrometers per year (μm/yr). Bulk chemical and surfacial end-point analyses of spent media and coupon surfaces showed preferential dissolution of nickel from Alloy 400 coupons and depletion of chromium from CRMs after incubation with YM bacteria. Scanning electron microscopy (SEM) also showed greater damage to the Alloy 400 surface than that indicated by electrochemical detection methods.

INTRODUCTION

The U.S. Department of Energy is engaged in a suitability study for a potential geological repository at Yucca Mountain, Nevada, for the containment and storage of commercially generated spent nuclear fuel and high-level nuclear waste. There is growing recognition of the role that microorganisms could play, in this repository, through MIC of waste packages and other repository components. Bacterial isolates from YM geologic material were shown in earlier studies to possess biochemical activities associated with MIC. Various microbial isolates demonstrated abilities to oxidize iron, produce sulfide, generate acids, and produce exopolysaccharides or “slime” layers on metal surfaces, thus establishing some potential for MIC in the potential repository’s environment [1].

A system was implemented to predict and quantify the contribution of YM bacteria to the overall corrosion of candidate WP materials by testing candidate WP materials under accelerated conditions employing sterile vs. nonsterile conditions. Using this approach, results from tests employing sterile conditions were compared to those conducted under nonsterile conditions, thus elucidating bacterial contributions to corrosion of specific materials. Overall corrosion rates were determined in the presence of characterized YM MIC-causing microbes or, in their absence, by

using well-accepted electrochemical polarization techniques. Subsequent end-point chemical analyses of spent aqueous media from these tests and surfacial analysis of exposed coupons further contributed to determining the mode and extent of MIC by YM bacteria.

EXPERIMENT

Electrochemical polarization data were generated in cylindrical glass flanges with O-ring seals; a working electrode sheet specimen was clamped to the O-ring, forming the bottom of the vessel (Figure 1). The total exposed area of the experimental coupon was 28.3 cm^2. A saturated calomel reference electrode was directly immersed in the cell along with a platinum counter electrode.

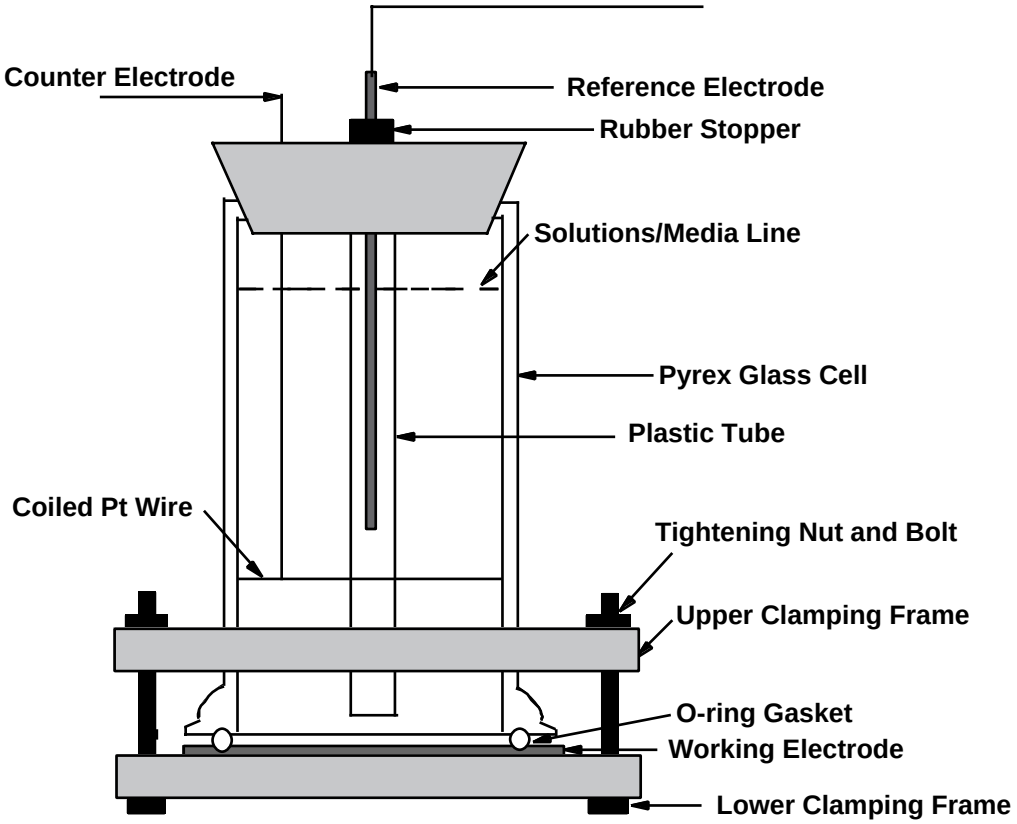

Figure 1. Corrosion vessel configuration for measurement of DC linear polarization in sterile or biotic environments

Working electrodes of C1020 carbon steel (UNS G10200), Alloy 400 (UNS N04400), Alloy 22 (UNS N06022), Alloy 625 (UNS N06625), and Type 304 Stainless Steel (SS304, UNS S30430) were wet-polished with abrasive paper progressively to 600-grit, cleaned with acetone and distilled water, and then sterilized by autoclaving before being inoculated with a mixture of 12 strains of YM bacteria, including acid, slime, sulfide producers, and iron-oxidizing bacteria [2]. Cell densities of all strains were determined; then at least 10^8 bacterial cells of each strain were aseptically combined, spread on material specimens, and finally air dried before being exposed to growth media in corrosion cells. Sterile control cells contained uninoculated working electrodes to assess abiotic corrosion effects.

The vessel was filled (450 ml) with R2 bacterial growth media, a low-nutrient formulation [3], supplemented with 0.5% glucose and 0.75% protease peptone #3 (Difco, Detroit, MI) in 100X simulated J13 groundwater (water from the vicinity of the YM site, [4]). The 100X simulated groundwater had the following components per liter of deionized water: 10.7g $NaHCO_3$, 0.32g NaF, 0.04g Na_2O_3Si, 0.05g $MgSO_4$, 1.67g Na_2SO_4, 0.88g $NaNO_3$, 0.64g KCl, 0.05g $CaCl_2$, 0.57g NaCl, and 0.02g H_2SO_4. All elements that came into contact with the growth media had been previously sterilized. All vessels were incubated at room temperature (approximately 22°C), and redox conditions in the vessels were at least initially aerobic. Experiments were conducted in a batch mode, whereby growth media was not renewed throughout the duration of incubation.

The DC linear polarization technique was periodically used to conduct polarization resistance (R_p) measurements in corrosion vessels. A potentiostat (EG&G Model 283) performed potential scans from 20 mV less than the corrosion potential (E_{corr}) to 20 mV greater than E_{corr} at a scan rate of 0.04 mV/sec. The R_p value was calculated by the EG&G Model 252/352 Softcorr II software.

Corrosion rates were calculated as current density (i_{corr}) in $\mu A/cm^2$ from the measured R_p [5]:

$$i_{corr} = B/R_p \qquad (1)$$

where

$$B = ß_a\, ß_c /2.303\, (ß_a + ß_c). \qquad (2)$$

$ß_a$ and $ß_c$ are known as anodic and cathodic Tafel constants, respectively (indicating activation polarization). $ß_a$ and $ß_c$ can be determined experimentally by polarization measurement. Polarization measurements showed $ß_a = ß_c = 0.15$ V/decade for the sterile carbon steel C1020, and $ß_a = 0.035$V/decade and $ß_c = 0.315$V/decade for C1020 inoculated cells. Undetermined ßa and ßc should not cause significant errors in calculated corrosion rates, and $ß_a = ß_c = 0.1$ V/decade are customarily used when ßa and $ß_c$ are unknown. Thus, for Alloy 400 and CRMs, the corrosion rate calculations were based on $ß_a = ß_c = 0.1$ V/decade. The i_{corr} was converted to corrosion rate (r) in micrometers per year (μm/y) as:

$$r = 3.277\, i_{corr}\, a/(n\, D) \qquad (3)$$

where a is atomic weight, n is equivalent number, and D is density.

After extended incubation with experimental metal coupons, aqueous spent media were analyzed by inductively coupled plasma (ICP) spectroscopy to determine the dissolution of metal alloying elements. To assess the extent of general corrosion and to determine elemental surface composition, scanning electron microscopy (SEM) with energy-dispersive spectral (EDS) analysis was performed on glutaraldehyde-fixed and dried coupons after exposure.

RESULTS

Comparison of corrosion rates deduced from experiments in corrosion vessels containing C1020 and Alloy 400 inoculated with YM bacteria to rates measured under sterile conditions showed that YM bacteria caused significantly increased corrosion rates on these materials (shown in Figure 2). After 5 months' exposure, a 5- to 6-fold increase in corrosion rate caused by YM bacteria was observed on C1020; a 100-fold increase in corrosion rate was observed on Alloy 400 because of microbial activities. As expected, the observed MIC rate of Alloy 400 was lower than that observed for C1020. However, the corrosion rate of Alloy 400 increased nearly twofold during the first two weeks of incubation, whereas the C1020 decreased. Thus, although there was an initial differential of 80-fold in MIC corrosion rate (0.31 μm/y for Alloy 400 and 24.89 μm/y for C1020), this was decreased to 7- to 8-fold after steady state was achieved (approximately 1.02 μm/y for Alloy 400 and 7.62 μm/y for C1020).

Corrosion rates for the corrosion-resistant materials (CRMs) Alloy 22, Alloy 625, and Type 304 stainless steel inoculated with YM bacteria were all measured below 0.04 μm/year (shown in Figure 3). Corrosion rates of these materials in sterile systems are currently being determined.

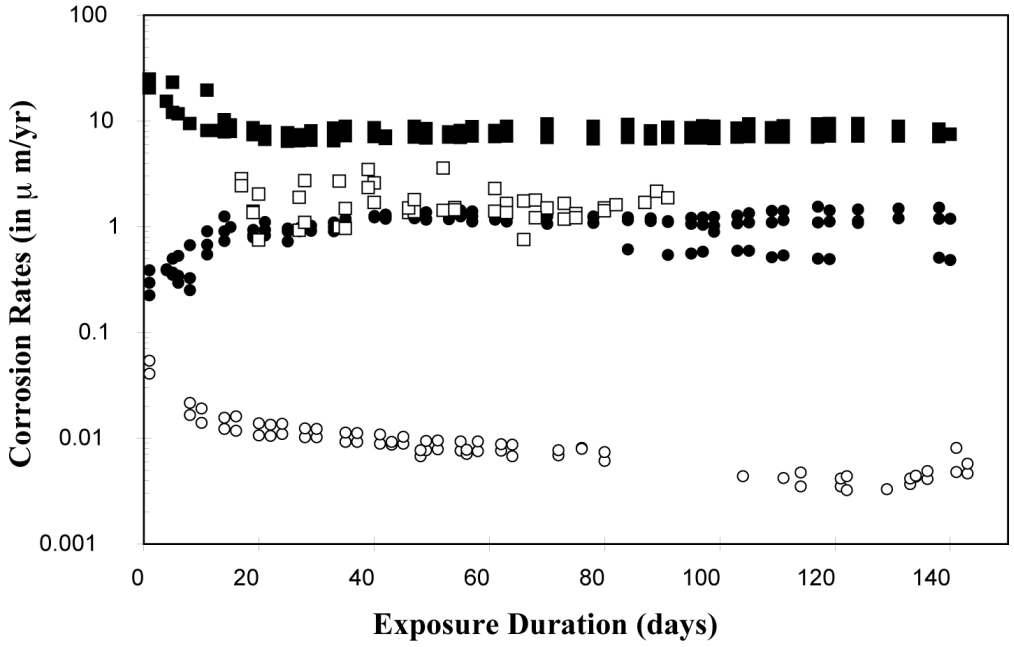

Figure 2. Corrosion rates measured by DC linear polarization of C1020 and Alloy 400 coupons inoculated with YM bacteria or left sterile.
■, C1020 with bacteria; ❑, C1020 with no bacteria; ●, Alloy 400 with bacteria; ○, Alloy 400 with no bacteria

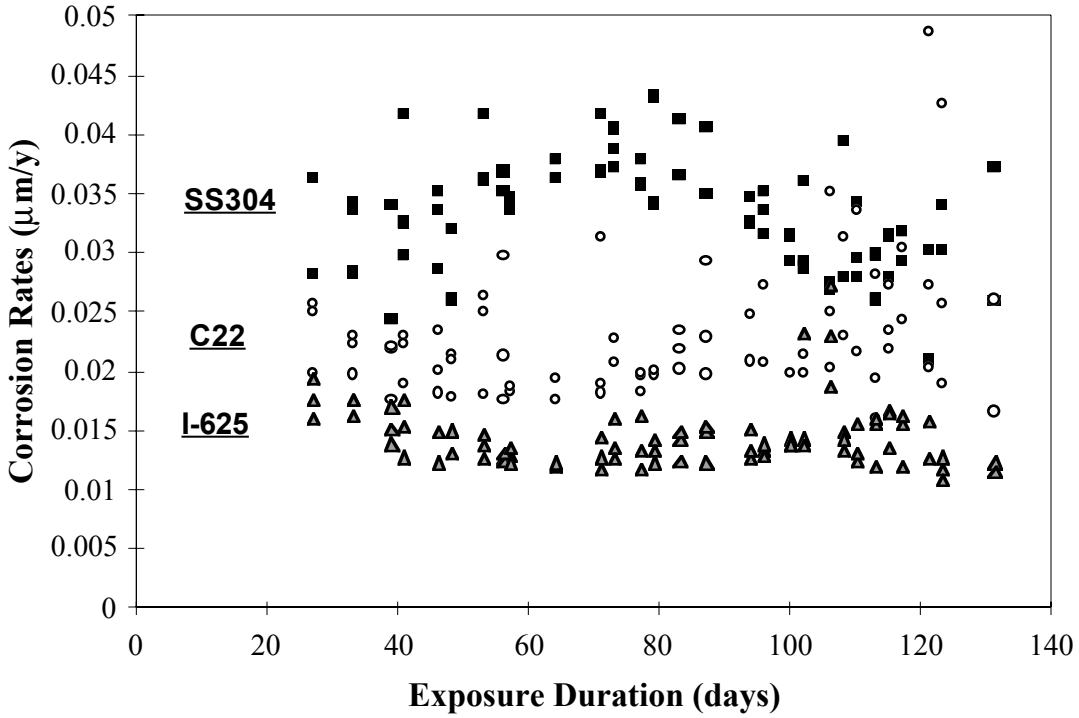

Figure 3. Corrosion rates measured by DC linear polarization of stainless steel 304, Alloy 22, and Alloy 625 coupons inoculated with YM bacteria.
■, SS304; ○, C22; ▲, I-625

After 5 months' incubation with inoculated bacteria, bulk aqueous phases from several cells containing different alloys were sampled and analyzed by ICP analysis for their total concentration of relevant metals (i.e., concentrations of both soluble and precipitated metals were determined). The ICP analytical results on bulk solutions from various cells are listed in Table I. The ICP analysis may underrepresent the actual corrosion rate, but it can be very helpful to determine if there has been significant preferential dissolution from the test alloys. Noteworthy is the observation that there was an almost 20-fold greater dissolution of nickel than of copper from Alloy 400 only when YM bacteria were present, indicating a de-alloying of the metal because of bacterial activities. Chromium depletion was observed from Alloy 22, Alloy 625, and Type 304 stainless steel coupons when these were inoculated with bacteria; however, their overall corrosion rates, as determined by linear polarization resistance, were low. Tungsten and Molybdenum concentrations in bulk solutions incubated with Alloy 22, Alloy 625, and Type 304 stainless steel were below levels of detection.

Table I. Accumulation of metals in media after exposure to YM bacteria

Vessel Conditions/Material	Cu (mg/l)	Fe (mg/l)	Cr (mg/l)	Ni (mg/l)
Unexposed media	n.d.*	0.25	n.d.	n.d.
No bacteria + Alloy 400	0.06	0.25	n/a**	0.09
Bacteria + C1020	n.d.	16.50	n/a	n.d.
Bacteria + Alloy 400	1.0	0.40	n/a	18.5
Bacteria + SS304	n.d.	0.57	1.03	0.04
Bacteria + Alloy 625	n.d.	0.33	1.07	0.12
Bacteria + Alloy 22	n.d.	0.32	1.05	0.1

*not determined ** not applicable

None of the candidate materials tested showed any pitting corrosion by gross visual examination after 5 months' exposure in the test environment. General corrosion was evident uniformly on the exposed surfaces of C1020 coupons, and dealloying was observed on Alloy 400 coupons. The de-alloying was supported by the discoloration of incubated Alloy 400 coupons in the presence of YM bacteria, where the preferential dissolution of Ni created a brown, copperlike appearance. Energy-dispersive spectral (EDS) analysis of incubated Alloy 400 revealed that the surface layer under the biofilm was indeed Cu-enriched (Figure 4) even though the initial Ni-Cu ratio in Alloy 400 was about 7:3. The SEM examination of incubated Alloy 400 also showed some degree of deterioration as demonstrated by a generalized flaking of the coupon surface (Figure 5).

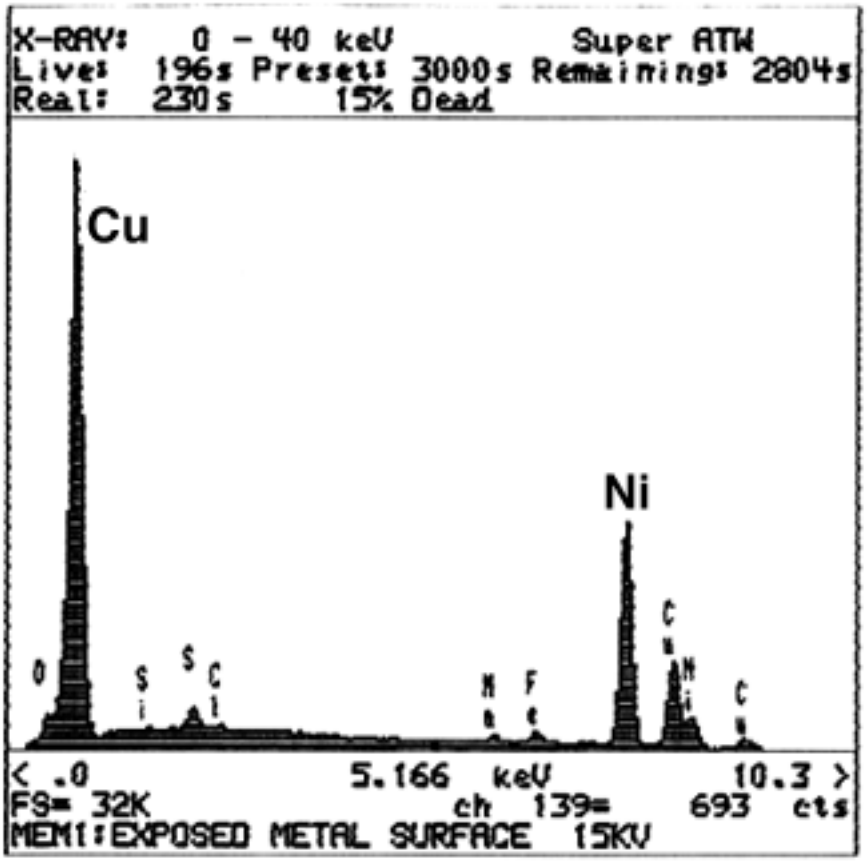

Figure 4. EDS analysis of Alloy 400 surface after 5 months' exposure to YM bacteria

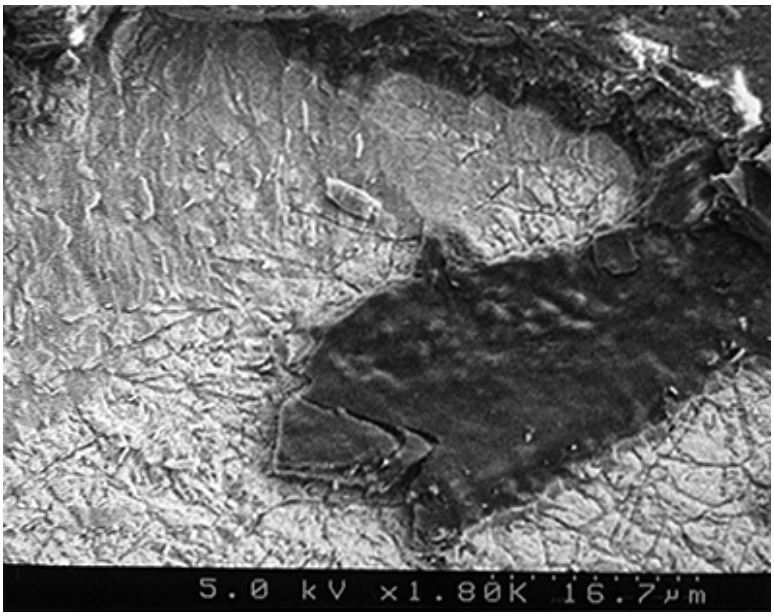

Figure 5. Scanning electromicrograph of the dealloyed surface of an Alloy 400 coupon after 5 months' exposure to YM bacteria

DISCUSSION AND CONCLUSIONS

The goals of these studies were to design and implement a system whereby the contribution of YM bacteria to overall corrosion rates of candidate WP alloys could be quantitatively determined. Further, we aimed to generate a system in which environmental factors could be altered and candidate alloys could be tested for their relative susceptibilities to MIC, and some mechanisms of MIC attack might also be discerned. Development of a novel corrosion cell permitted the evaluation of MIC of corrosion-resistant WP candidate materials. However, because the coupon was entirely submerged in the vessel, and the media remained unaerated throughout the incubation period, electrochemical conditions at the coupon surface were assumed to be uniform and anoxic because oxygen was presumably progressively consumed by aerobic microbial activities in this system. Thus, enhancing of differential oxygen concentrations by microbial activities was not observed, and corrosion rates were correspondingly low. Future modifications to this system will therefore include periodic or continual aeration of the media to better simulate projected conditions at the potential YM repository.

Measured rates of corrosion on both inoculated and sterile coupons changed during the incubation period until they reached a "steady-state" value. Initial elevated rates on inoculated C1020 coupons may reflect the ready availability of nutrients and oxygen. Lower rates observed later in the incubation period could indicate exhaustion of the media and oxygen immediately surrounding the alloy coupon or the buildup of toxic end products. Because diffusion of nutrients and end products would be minimal, it is expected that the observed steady state may not reflect that which would occur in a continuously fed system, which would better reflect actual repository conditions and provide a better measure of MIC over the long term.

Despite these caveats, it was possible, using this system, to discern a 5- to 6-fold increase in corrosion caused by inoculated bacteria to carbon steel coupons and nearly a 100-fold increase in corrosion rates on Alloy 400. Corrosion rates on CRMs were on the order of hundredths of µm/year; however, because SS304 is well known to be susceptible to microbially induced pitting (and this was not observed in this system), it is clear that conditions were not wholly conducive

for inducing MIC of these materials. Planned alterations to this system, which will also be more representative of repository conditions, include a continuous supply of media that better simulates YM groundwater, incorporation of YM rock, and oxygenation and mixing of introduced media. These experimental iterations will not only more closely emulate anticipated repository conditions, but should also be more aggressive and thus may induce more severe MIC on CRMs.

Bulk chemical and surfacial end-point analyses of spent media and coupon surfaces showed preferential dissolution of nickel from Alloy 400 coupons; this observation was supported by surfacial EDS analyses of the coupons after incubation with YM bacteria. SEM also showed greater damage to the Alloy 400 surface than that indicated by electrochemical detection methods; striation and flaking of the coupon surface were evident. Further, chromium was detected in bulk solutions incubated with inoculated CRM coupons.

ACKNOWLEDGMENTS

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